

# **Predicting range UXO source quantity and its impact on future training**

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## **Abstract**

A model has been developed to estimate the source quantity of UXO for use as a source term model within the Army Risk Assessment Modeling System (ARAMS). ARAMS is based on the widely accepted risk paradigm, where exposure and effects assessments are integrated to characterize risk. ARAMS allows the UXO model to be readily used as a component in human and/or ecological health risk characterizations for estimating the mass of explosives that is needed as information to drive media fate/transport models, such as leaching through the vadose zone and runoff into surface waters. Calculated temporal media concentrations are then used within ARAMS to compute exposure and assess effects both current and future.

The UXO model provides an estimate of the source quantity of UXO using data from firing range records and other sources. The model is an enhancement of the Multimedia Environmental Pollutant Assessment System (MEPAS) Computed Source Term Release Model. The output from the UXO model can be used with other components of the ARAMS modeling system to compute human and/or ecological health risk from exposure to the UXO and therefore allows site planning and management to be adjusted for range sustainment and future training needs. An added benefit of using ARAMS is that it inherently allows uncertainty to be performed on the UXO model's input parameters.

This paper describes both the development of a model to predict the source quantity of UXO and an example human health risk characterization that shows how the model can be readily used to characterize human health risks associated with exposure to UXO which range management could then use to plan future training activities.

*Keywords: munitions emissions, UXO, energetic materials, human health characterization, firing ranges, ARAMS, MEPAS, fate and transport modeling.*

## **1 Introduction**

The 1997 UXO Clearance Report to Congress estimated that millions of square meters throughout the United States, including 1,900 Formerly Used Defense Sites (FUDS) and 130 Base Realignment and Closure (BRAC) installations, potentially contain unexploded ordnance (UXO) and explosives contaminants. In addition, testing and training ranges which are essential to maintaining the readiness of the Armed Forces of the United States contain both UXO and munitions residues such as explosives. Recently, concerns have arisen over potential environmental contamination from residues of energetic materials at impact ranges. A key to sustaining training at firing ranges is the ability to determine environmental impacts of range activities and perform the exposure assessment phase of risk assessments for present and future training activities.

No comprehensive study has yet been undertaken to characterize the quantities, transport properties, or outcomes of energetic materials and their by-products in the environment. The task of identifying the extent of contamination becomes complicated when the contaminants are energetic materials. Energetic materials do not behave like other known soil or water contaminants and can pose a significant hazard when UXO is also present (Thiboutot, Ampleman, and Hewitt [1]).

## **2 Modeling Approach**

The general steps required of the UXO source term model to quantify explosives source material include the following:

- Estimate residue mass of explosive compounds for source area (i.e., the range impact area or area of concern).
- Estimate surface area to mass ratios of explosives residue required for dissolution.
- Calculate dissolution rates of solid phase explosives residues.
- Estimate soil fate process coefficients, i.e., sorption distribution coefficient and transformation rate, for aqueous phase of explosive residues.
- Compute fate/transport pathway fluxes from the source area and remaining soil concentrations within the source area.

Each of these steps is discussed below in the context of how each is handled in the UXO source term model.

### **2.1 Estimation of Mass of Explosives from UXO**

Brannon et al. [2], presented a method for determining the number of UXO potentially contributing to the contaminant source term. UXO contributions arise from duds, low-order detonations, and high-order detonations or blasts. The amount of explosive from UXO can be estimated from the number of munitions of each type fired, the dud percentage, low-order detonation percentage, percent yield, signature spread and blast contribution. Signature

spread (areal extent of explosive residue) is currently a placeholder in the model until additional information can be obtained on how it should be incorporated into the model. The dud percentage can be used to get an estimate of the number of rounds that did not detonate and are subject to corrosion. The number of UXO associated with duds is estimated from eqn (1)

$$UXO_{dud\_j} = \frac{N_{fired\_j} * D_{perc\_j}}{100.0} \quad (1)$$

where,  $UXO_{dud\_j}$  is the number of UXO contributed to duds for munition type  $j$ ,  $N_{fired\_j}$  is the total number of rounds of munitions of type  $j$  fired, and  $D_{perc\_j}$  is the dud percentage for munition type  $j$  (percent).

Dud rounds are “potential” source contributors because they must first undergo breakage or corrosion. Explosive contamination from broken or corroded munitions is not currently computed in the model because of the lack of data for these sources. Thus, duds are not presently considered as contributors of UXO in the model. However, the model has placeholders, which can later be populated with an algorithm once sufficient data have been obtained for modeling these contributions. The model has the capability to check for the type of munitions, which could be used to determine which munitions are more susceptible to corrosion or breakage and thus providing a corrosion or breakage component to the mass of explosives. The U.S. Army Environmental Center, Maryland, is developing a model to determine UXO corrosion in soils under various redox potential, soil moisture, and pH (Owens [3], Packer [4]).

Field sampling has shown that low-order detonations are the major source of explosives contamination on firing ranges (Pennington et al. [5]). High-order detonation mass loadings can be estimated from the numbers of each type round fired, less any duds and low-order rounds, multiplied by the percentage of high-order detonations. When range firing records are not available or incomplete, the user will need to provide an estimate for the number of munitions of each type fired. Dud and low-order percentage are available for most Army munitions (Dauphin and Doyle [6]; [7]). If these parameters are unavailable for specific munitions, estimates will be needed for all of these parameters. Equations to compute numbers given estimates of parameters are provided herein.

The low-order detonation percentage is used with the total number of rounds of each munition fired to obtain an estimate of the number of UXO that underwent incomplete detonations as shown in eqn (2)

$$UXO_{LO\_j} = \frac{N_{fired\_j} * LO_{perc\_j}}{100.0} \quad (2)$$

where,  $UXO_{LO\_j}$  is the number of UXO contributed to low-order detonations for munitions type  $j$ ,  $LO_{perc\_j}$  is the low-order detonation percentage for munitions type  $j$  (percent) and all other terms are as previously defined.

The mass of each explosive in each munition due to low-order detonations can be obtained by computing the sum of each of the explosives in each munition as shown in eqn (3)

$$M_{LO\_i} = \sum_{j=1}^{j=n} MM_{i,j} * UXO_{LO\_j} * \left( \frac{100.0 - Yield_j}{100.0} \right) \quad (3)$$

where,  $M_{LO\_i}$  is the mass of explosive  $i$  contributed to low-order detonations, (kg)  $Yield_j$  is the yield for low-order detonations of munition type  $j$  (percent),  $MM_{i,j}$  is the mass of explosive  $i$  contained in munition  $j$  (kg),  $n$  is the number of different munition types, and all other terms are as previously defined.

The mass of explosives from UXO contributed to blasts (high-order detonations) can be estimated as shown in eqn (4)

$$M_{BC\_i} = \sum_{j=1}^{j=n} \left[ MM_{i,j} * N_{fired\_j} * \left( \frac{100 - D_{perc\_j} - LO_{perc\_j}}{100} \right) * \frac{BC_{i,j}}{100} \right] \quad (4)$$

where,  $M_{BC\_i}$  is the mass of explosive  $i$  contributed to the blast effect of the munition detonation (kg),  $BC_{i,j}$  is the UXO blast contribution for explosive  $i$  from munition type  $j$  (percent), and all other terms are as previously defined.

Assumptions for use in the model are summarized as follows. It is assumed that mortar and artillery rounds that have not been broken or undergone low-order detonations retain their explosive contents within the delivery system until corroded. This assumption is based on the relatively thick casings of the munitions, especially artillery shells. Thus, the only mass currently considered in the source term from these rounds is that from low-order detonations and blast contributions for high-order detonations. Low-order detonations and blast contributions are assumed to be evenly distributed over the area chosen to model. Low-order detonations, which are the only type that require percent yield information, are assumed to have a 10% yield with the remainder of the main charge deposited as a powder in the absence of other information. Signature spread is a placeholder at this time. If firing records are available, then these records should directly indicate the dud percentages, low-order percentages, and high-order blast contributions based on the number of each type round fired on the range.

## 2.2 Estimation of Surface Area to Mass Ratios

A key to modeling the dissolution of explosives and their subsequent fate and transport on firing ranges is estimating the surface area to mass ratios of explosives deposited on firing ranges. The ratio of exposed explosive residue mass surface area to the total explosive residue mass distributed over a site are calculated based on information from Lynch, Brannon, and Delfino [8], who measured the surface area to mass ratios for military grade TNT, RDX, HMX, and the military formulation LX-14. The model assumes residue mass is uniformly distributed over the site area.

Information on explosives particle sizes on test and firing ranges is extremely limited, although more is being generated in controlled tests (Pennington et al. [5]). Radke, Gianotto, and Roberto [9] examined articles of explosives at a historical testing range (last used over 50 years ago) and found

that TNT particles larger than 3mm accounted for 96.4% of the explosives contamination at the site. From the data in their paper and the data in Lynch, Brannon, and Delfino [8], surface area to mass ratios were developed based on the average particle weight (Table 1). Data in Table 1 for Radke, Gianotto, and Roberto [9] used an average size of particles of 0.087 g.

Table 1: Surface area to mass ratios.

Explosive	cm <sup>2</sup> · g <sup>-1</sup>
TNT	2.02
RDX	8.73
HMX	52.06
Octol HMX	HMX Powder = 36.4 HMX Pellet = 1.42
Octol TNT	TNT Powder = 15.6 TNT Pellet = 0.6
Comp B RDX	RDX Powder = 5.2 RDX Pellet = 1.2
Comp B TNT	TNT Powder = 3.5 TNT Pellet = 0.8
LX-14 HMX	LX-14 pellets = 0.9

### 2.3 Calculation of Dissolution Rates of Explosive Residues

Aqueous dissolution of explosives residues is affected by solid residue surface area, ambient water temperature, water mixing rate, and pH. Studies (Lynch et al. [10] and Lynch, Brannon, and Delfino [8]) showed that mixing rate and pH had much less effect on dissolution than surface area and temperature. Thus, the dissolution rate can be expressed (Lynch, Brannon, and Delfino [11]) as shown in eqn (5) for explosives compounds,

$$\frac{dm}{dt} = a(\beta e^{\theta T}) \quad (5)$$

where, dm/dt is the explosive mass dissolution rate (mg/sec), a is the solid mass surface area (cm<sup>2</sup>), T is the water temperature (deg C), and β, θ are empirical coefficients for temperature effects.

The empirical temperature coefficients vary for TNT, HMX, and RDX for pure compounds and for formulations. Values for β and θ reported by Lynch, Brannon, and Delfino [11] for a median mixing rate of 150 rpm are shown in Table 2. Eqn (5) is used within the fate/transport model section along with the appropriate temperature coefficients in Table 2 for the formulation/explosive being evaluated. After estimating total explosive residue mass as described previously, the total mass is used to estimate the surface area, a, as described in the previous section, and the surface area is used in eqn (5) to estimate dissolution rate given the temperature.

Table 2: Coefficients for explosive residue dissolution rate equation.

Explosive	$\beta$	$\theta$
Pure compound		
TNT	$7 \times 10^{-5}$	0.0755
RDX	$1 \times 10^{-5}$	0.0762
HMX	$5 \times 10^{-5}$	0.0635
Formulation compounds		
Octol – TNT	$3 \times 10^{-5}$	0.0769
Octol – RDX	$1 \times 10^{-6}$	0.0728
Comp B – TNT	$3 \times 10^{-5}$	0.0690
Comp B – RDX	$7 \times 10^{-6}$	0.0574
LX-14 - HMX	$2 \times 10^{-6}$	0.0903

## 2.4 Process Coefficient Selection

No empirical relationships have been defined between either explosives adsorption coefficient ( $K_d$ ) or transformation rate coefficients ( $K$ ) and soil properties that can be used to determine the appropriate coefficient for a specific situation. The data tabulated in Brannon and Pennington [12], was therefore examined to determine if the selection of appropriate coefficients could be simplified by associating ranges of values with ranges of soil properties.

### 2.4.1 Selection of $K_d$ Values

Examination of the data summarized in Brannon and Pennington [12] showed that simplification of the coefficient selection process for TNT, RDX, and HMX could be furthered by arbitrarily dividing the  $K_d$  values on the basis of high, medium, and low ranges of the following soil parameters: % clay, cation exchange capacity (CEC), and total organic carbon (TOC). Ranges of values and the mean ( $\pm$  standard error) of  $K_d$  associated with ranges of soil characteristics are provided in Table 3 for TNT and RDX.

Table 3: Ranges and mean values of soil partitioning coefficients for TNT and RDX.

% clay	CEC, milliequivalents $\cdot g^{-1}$	TOC, %	Range of $K_d$ values, $L \cdot kg^{-1}$	Mean $K_d$ (standard error)	Number of observations
TNT					
0-20	0-10	0-1	1.04-3.64	0.88 (0.31)	11
20-50	11-30	1-3	2.3-6.16	3.39 (0.32)	14
> 50	> 30	> 3	2.23-11	5.54 (0.77)	12
RDX					
0-20	0-10	0-1	0.07-1.57	0.53 (0.14)	11
20-50	11-30	1-3	0.06-1.65	0.85 (0.15)	13
> 50	> 30	> 3	0.31-8.4	2.31 (0.63)	15

#### 2.4.2 Selection of Transformation Rate Coefficients

Examination of transformation rate coefficients for TNT, RDX, and HMX and their transformation products tabulated in Brannon and Pennington [12] showed that redox condition (aerobic or anaerobic) and total organic carbon (TOC) content were the main determinants of transformation rates. Ranges and means of transformation rate constants for TNT, RDX, and HMX under aerobic conditions are provided in Table 4. Transformation rates can be converted to half-lives by using the formula in eqn (6)

$$t_{1/2} = \frac{0.693}{K} \quad (6)$$

where,  $t_{1/2}$  is the half-life (hr) and K is the first-order transformation rate coefficient ( $\text{hr}^{-1}$ ).

Table 4: Ranges and mean values of soil transformation rate coefficients for TNT, RDX, and HMX

TOC, %	Range of Transformation Rates ( $\text{hr}^{-1}$ )	Mean (SE) of Transformation Rates ( $\text{hr}^{-1}$ )	Number of Observations
TNT (Aerobic)			
0-1	0-0.144	0.03 (0.023)	6
>1	0.013-0.162	0.064 (0.049)	3
RDX (Aerobic)			
0-1	0-0.008	0.0047 (0.0024)	3
>1	0.008-0.0163	0.011 (0.0028)	3
HMX (Aerobic)			
0-1	0-0.004	*	2
>1	0-0.0163	*	2
* Mean and standard error are not provided when only two observations are available.			

#### 2.5 Fate/Transport Model

The fate/transport model is based upon the Multimedia Environmental Pollutant Assessment System (MEPAS) Computed Source Term Release Model (CSTRM). MEPAS is a suite of models that address fate/transport in various environmental media (air, surface water, vadose zone, groundwater, and food items) and human exposure pathways, uptake, and health impacts. The MEPAS models provide much of the exposure assessment modeling capabilities within ARAMS.

The CSTRM (Streile et al. [13]) computes contaminant loss from three types of source zones: aquifers, pond or surface water, and soil/vadose zone. The soil/vadose zone component was used for the UXO model. Contaminant mass loss pathways include degradation, leaching, wind suspension, water erosion, overland flow, and volatilization. The system of first-order, ordinary, differential equations for mass fluxes are numerically solved with a fourth-order Runge-Kutta method using an annual time-step. The model calculates the

appropriate mass lost to each pathway and the mass remaining in the source zone.

For the UXO model, the CSTRM was modified to include a solid phase component and an algorithm for computing dissolution along with appropriate user-interface changes for the new inputs required.

### 3 Example Application

This application is a simple hypothetical example of future training on a range. Scenario “A” has twice as many rounds fired per year as Scenario “B” for a given type of munition(s). It is assumed that the rounds fired in each scenario are evenly distributed over the site. The range will be used for 50 years. We would like to know how individual excess cancer risk might be used to adjust future training on the range based on these two scenarios. The receptor is an adult individual who visits the site for 8 hours a day, 38 days a year, for 30 years. The constituent of concern is TNT. The exposure pathways are soil ingestion, dermal contact with soil, and soil inhalation. The schematic of this modeling scenario and the ARAMS conceptual site module interface are shown in fig.1 and fig. 2, respectively. The incremental cancer risks are shown in fig. 3 for both scenarios. Note the excess cancer risk for scenario “A” is greater than scenario “B”, which may play a role in evaluation of future training.

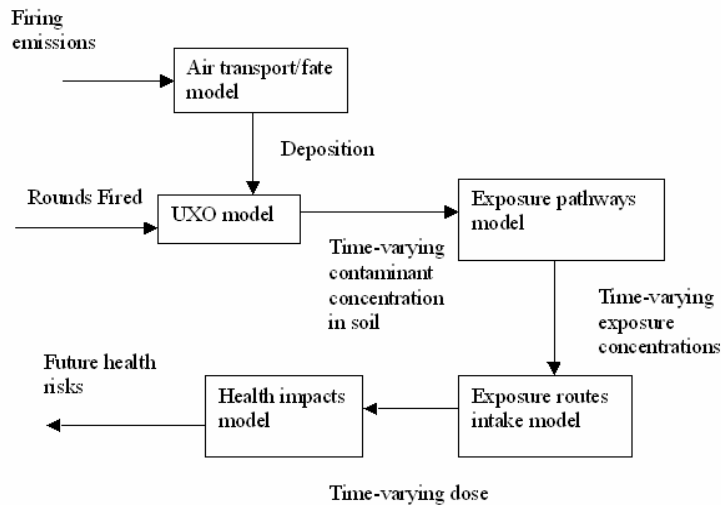


Figure 1: Modeling scenario schematic.



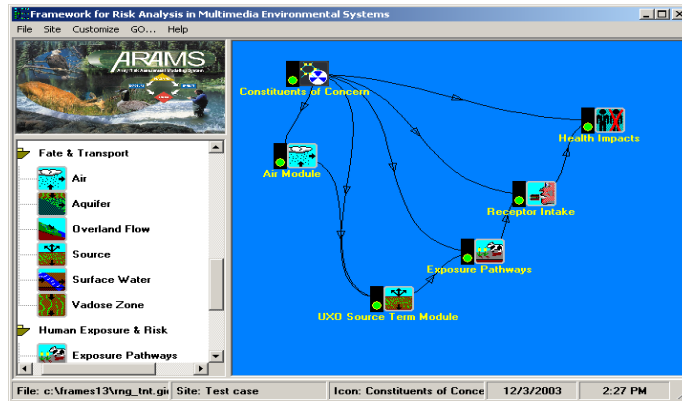


Figure 2: ARAMS conceptual site model interface for scenarios.

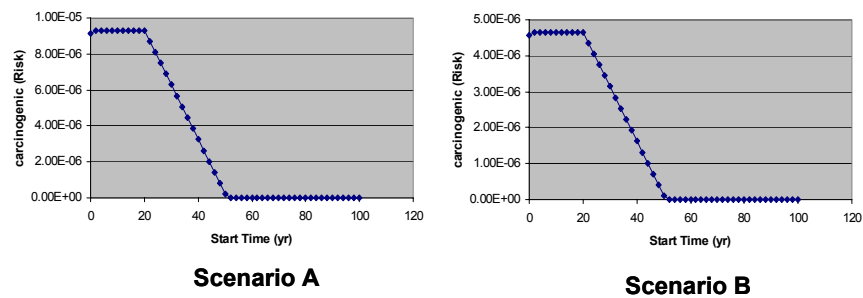


Figure 3: Incremental cancer risk for scenarios "A" and "B".

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